

**Title:** Development of Analytical Methods for Comprehensive Chemical and Physical Speciation of Arsenicals in Groundwater

**Project I.D.:** DNR Project Number #154

**Investigators:** Principal Investigator – Joseph Aldstadt, Assistant Professor, Dept. of Chemistry, Univ. of Wisconsin-Milwaukee, 3210 N. Cramer St., Milwaukee, WI 53211

Research Assistants — Rebecca Johnson, Jon Scaffidi, Aaron Roerdink, Jason Harb, Dept. of Chemistry, Univ. of Wisconsin-Milwaukee, 3210 N. Cramer St., Milwaukee, WI 53211

Project Assistant (Visiting Professor) — Christine Blaine, Department of Chemistry, Carthage College, 2001 Alford Park Drive, Kenosha, WI 53140

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**Background/Need:** The basis for understanding the abundance and distribution of arsenic in groundwater is reliable chemical analysis. Improvements in sample collection, sample pre-treatment, and on-site and off-site laboratory determination methods are sought to insure that information about arsenic is accurate and precise.

**Objectives:** The objective of this project was to develop analytical methods that could be used to comprehensively characterize the specific chemical and physical forms of arsenic that are present in groundwater formations found in the Fox River Valley (FRV).

**Methods:** The primary arsenic compounds present in Fox River Valley groundwater are the trivalent and pentavalent oxyacids, arsenious and arsenic acids, respectively. These compounds are found predominantly as dissolved species (solution phase) but also adsorbed to small particles and colloidal matter (particulate phase). Sample collection by solid-phase extraction, sample pretreatment by use of iron-chelating preservatives, on-site analyte determination by potentiometric stripping, off-site analyte determination by ion chromatography, and (on-site and off-site), and physical characterization field-flow fractionation were studied.

**Results and Discussion:** For **sample collection**, we optimized an existing method based on Solid-Phase Extraction (SPE) (X.C. Le, S. Yalcin, M. Ma. *Environ. Sci. Technol.* **2000**, *34*, 2342). Arsenite and arsenate are quantitatively sampled from groundwater samples using a method in which anion-exchange cartridges allow for the removal of matrix interferences and pre-concentration of the analytes. We conducted three field sampling exercises in which we studied the sampling method conditions. Analysis was then performed off-site using inductively-coupled plasma mass spectrometry (ICP-MS). This effort culminated in the design, fabrication, and field-testing of a suitcase-sized “kit” to facilitate the convenient use of this method with high precision and accuracy.

For **sample pre-treatment**, we developed an improved method for the preservation of inorganic arsenicals in iron-rich water samples. The method is designed to chelate Fe(III) ions in solution because: (a) Fe(III) can rapidly oxidize As(III) to As(V), and (b) As(V) is quickly and tenaciously adsorbed by iron

oxyhydroxides (colloidal FeOOH species) during a complex co-precipitation process. Precipitation of As(V) during sample transport and storage prior to off-site analysis introduces a “false negative” bias in the analytical accuracy because precipitates are commonly filtered off prior to off-site analysis. Ethylene diamine tetraacetic acid (EDTA) has been recently reported in the literature by several laboratories as an effective reagent for Fe chelation in arsenic analysis. We studied several other well known Fe-chelants that possess higher formation constants for the complexation of iron species and can be used optimally at neutral pH. We developed and optimized a method using either Oxine or Cupferron that showed a ~20% improvement in As recovery relative to reported EDTA-based methods.

For **on-site (field-portable) determination of arsenite/arsenate**, we developed and tested a field-portable instrument and method based on potentiometric stripping analysis (PSA). This technique allows for the chemical speciation of the arsenicals immediately after sample collection (i.e., to quantify the dissolved forms). Detection limits are <1 part per billion (ppb) for each form of inorganic arsenic with the measurement taking <45 min to complete. The advantage of the on-site method is that it can minimize errors that are commonly introduced by sample handling, transport, and storage prior to conventional off-site laboratory analysis.

For **off-site (laboratory) determination of arsenite/arsenate**, we developed and optimized a high-resolution laboratory method based on Ion Chromatography (IC) with optical detection. Although ICP-MS with chromatographic “front-ends” such as IC are used in research laboratories for the chemical speciation of arsenic, for *practical* implementation of the new EPA standard of 10 µg/L by municipal water treatment labs, IC with optical detection provides significant advantages because the capital and operating costs are drastically less than ICP-MS. Furthermore, IC with optical detection permits direct speciation of arsenite and arsenate at relevant levels with high selectivity. Method detection limits are comparable to the PSA method but with better rejection of possible interferences because of the chromatographic process.

For **physical characterization**, we setup a flow field-flow fractionation (Flow FFF) system and studied a method to quantify the arsenicals in the small particle phase (50-500 nm) in groundwater samples. These species are often omitted in conventional (solution phase) analysis but can still be found in drinking waters because they are small enough to pass through typical filtration systems. Fluorescence and light-scattering detectors were used to study the separated zones. Direct coupling of the Flow FFF instrument to ICP-MS shows promise for examination of the physical speciation of arsenic.

## **Conclusions/ Implications:**

Our work has shown that solid-phase extraction (SPE) is an effective method for on-site sample collection when information on the chemical speciation of arsenite and arsenate is desired. For samples in which “total (inorganic) arsenic” information is sought, Oxine or Cupferron appear to be more effective than EDTA in preserving the dissolved arsenic oxyanions. Both sample collection methods require further field-testing statewide to determine their robustness.

For the on-site quantitation of arsenite and arsenate, the potentiometric stripping analysis (PSA) method has the requisite sensitivity and selectivity. However, the requirement to heat the sample to 95 °C (for arsenate reduction) is impractical — incorporation of an automated flow-injection type heating module would be a straightforward way to make it more convenient to use in the field.

The method for off-site analysis by ion chromatography with optical detection is an excellent method for off-site quantitation of arsenite and arsenate. Validation of the IC method using NIST standards at the new drinking water standard (10 ppb) has the potential to facilitate nation-wide implementation of the new 10 ppb As standard.

Flow field-flow fractionation (Flow FFF) coupled on-line to ICP-MS has the potential for developing a better understanding of arsenic:particle distributions. The method requires a significant effort to minimize the aggregation of particles and should benefit from the preservation chemistry that was also studied as part of the project.

- Publications:** R.L. Johnson, J.H. Aldstadt. "Quantitative Trace-Level Speciation of Arsenite and Arsenate in Drinking Water by Ion Chromatography", *The Analyst (London)* **2002**, 127, 1305-1311.
- Key Words:** Arsenic, arsenite, arsenate, ion chromatography, potentiometric stripping, solid-phase extraction, field-flow fractionation
- Funding:** Wisconsin Department of Natural Resources
- Final Report:** A final report containing more detailed information on this project is available for loan at the Water Resources Institute Library, University of Wisconsin - Madison, 1975 Willow Drive, Madison, Wisconsin 53706 (608) 262-3069.